Experimental Study on the Kinetics of Sintering of Metal Powder at Constant Temperature. II

Experimental Study on the Kinetics of Sintering of Metal Powder at Constant Temperature. II*

Yoshimichi MASUDA and Sadao KIKUTA

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The densification rate of various compacts of some metal powders, such as silver, iron, and nickel during sintering, was studied with particular reference to the characteristics of powder and to the temperature.

The behaviour of the densification rates of those metal powder compacts at constant temperature was expressed approximately by a simple power relation, at least in a steady-progressive range of sintering process, as well as in the case of sintering of copper powder compact.

On the basis of the empirical formula between the fraction of total decrease in volume of pores in a compact and the sintering time, an investigation was made by the same experimental techniques as those in the previous work on the influences of sort of metal and powder, of pressing load or initial density of compact, and of other sintering conditions, upon the rate of densification.

From the results obtained, it was explained qualitatively that the rate of densification of powder compact in isothermal sintering process depends most intensively on the geometrical characteristics of powder ; that a little difference in pressing load or initial density of compact does not introduce any effect upon the rate of densification.

Temperature dependence of the rate of desification in a range of moderate temperature was confirmed to be approximately exponential to absolute temperature over all these metal powders, if the systematic deviation from this relation at high temperature could be ignored.

The heats of activation in this process, obtained from this relation, were of the same order as that for self-diffusion of these metal atoms. Moreover, it was found that the densification processes in the different powder compacts of same metal produced by different processes were governed by different heats of activation which were nearly independent of other sintering conditions.

In addition, a general tendency of lowering the activation heat towards high temperature was observed for the same powder compact of same metal. In this paper, however, this result was not stressed because of little reliability of the experimental data for the rate of densification at high temperature.

I. Introduction

In powder metallurgy, it is an important problem to elucidate the principal

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process and mechanism of metallic sintering, which involves an approach to certain fundamental questions in the field of metal physics, such as surface tension, diffusion, creep and crystal growth.

The small droplets of metals brought in contact with one another are usually bound only by heating without any application of external forces under any particular set of condition. The binding process is naturally motivated by surface tension, but, for the transportation of materials taken place there, many different mechanisms have been proposed by a number of investigators[1]; they propose, for example, diffusion, creep, crystal growth, and evaporation and condensation. A lively discussion on this question has been going on among them for years after the war, and has not yet come to a conclusion by this time. One of these investigators, Kuczynski[2] treated mathematically the rate of binding taken place between a plate and a small droplet or a thin wire of metal, and the experimental verifications were carried out by his collaborators.[5] The others, Shaler and Wulff[4], also studied the same problem from the other point of view and made much contribution to understanding of the sintering mechanism as well as the former.

There are, on the other hand, a number of studies which are undertaken from a stand-point of chemical reaction rate, on the sintering of compact produced by commercial metal powder. The results of these works are also available for the explanation of kinetics and mechanism of sintering as well as for the practice of powder metallurgy.

The works dealing with this concept were recently published independly of one another by Jordan and Duwetz[5] in America, by Hüttig and his school[6] in Germany, and by the authors[7] in Japan almost at the same time in 1949.

In our previous paper cited above, there are included some experimental results and the interpretation of sintering rate, dealing with breaking strength and densification of sintered compact at various constant temperature for copper and iron powder. The values of activation heat for densification of these metal powders during sintering, which were estimated from the temperature dependencies of the densification parameter, were given in good agreement with those for self-diffusion obtained by other methods. It was, therefore, suggested that the densification of metal compact during sintering could be governed by the same mechanism with those of the self-diffusion of atoms or vacancies. In order to make further approach to this point, a systematic and detailed knowledge of the change in densification rate

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(1) P. Schwarzkopf: Powder Metallurgy. The Macmillan Co., New York (1947).
(2) G. W. Kuczynski: J. of Metals (1949), 169 TP 2528; J. of Applied Phys. 21 July (1950) 632.
(3) J. H. Dedrick, A Gerds: J. of Applied Phys. 20 Nov. (1949) 1042.
(4) A. J. Shaler: J. of Met., I (1949) 796.
(5) C. B. Jordan, P. Duwez: J. Met., I (1949) 96.
(6) G. F. Hüttig: Z. f. Elektrochem. **54** (1950) 88.
(7) T. Okamura, Y. Masuda, S. Kikuta: Sci. Rep. RITU, 1 A (1949) 357.

with characteristics of powder compacts and sintering conditions was required. For this purpose, the present work was undertaken for various types of metal powder compacts. The main procedure in experimental techniques and treatment of the results were almost the same as the previous work.

II. Materials and Preparations

Powders

Various types of metal powders of silver, iron, and nickel were used for this work, which were produced by different procedures. In order to make a strict comparison between sintering process for each sort of metal powder, it must be of the same characteristic powder produced by the same procedure in all works. In fact, however, it is difficult to satisfy throughly this requirement because of the difference in chemical and physical properties of each metal, and, therefore, the applicable way of disintegration to these metals is limited. Accordingly, each powder was prepared by various ways as described below.

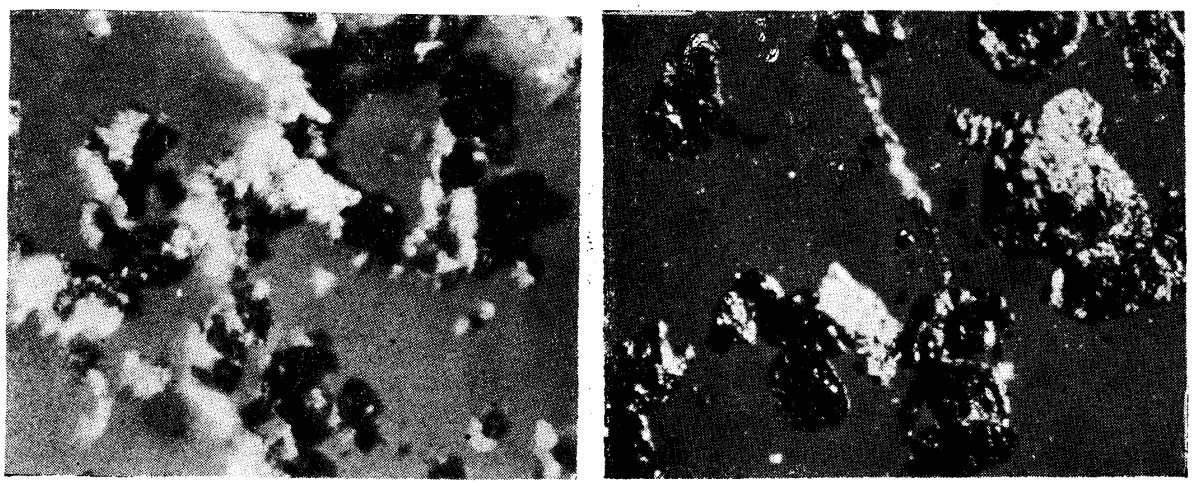
Silver :

The powders of this metal were prepared by a mechanical disintegration from the chips, which were produced by machining the ingot with a metal saw. The powder (A) was produced by a stamp-mill, and the other (B) by a Eddy-mill[8], and before being used, the both powders were passed through a 200 mesh screen. They were all —200 mesh and coarser in particle size than the other powders (of iron and nickel), though they were of the highest purity available. The portion of the fine powder of —325 mesh was less than 10 pct of the total. Their microphotographs are shown in Fig. 1. (A), (B).

Iron :

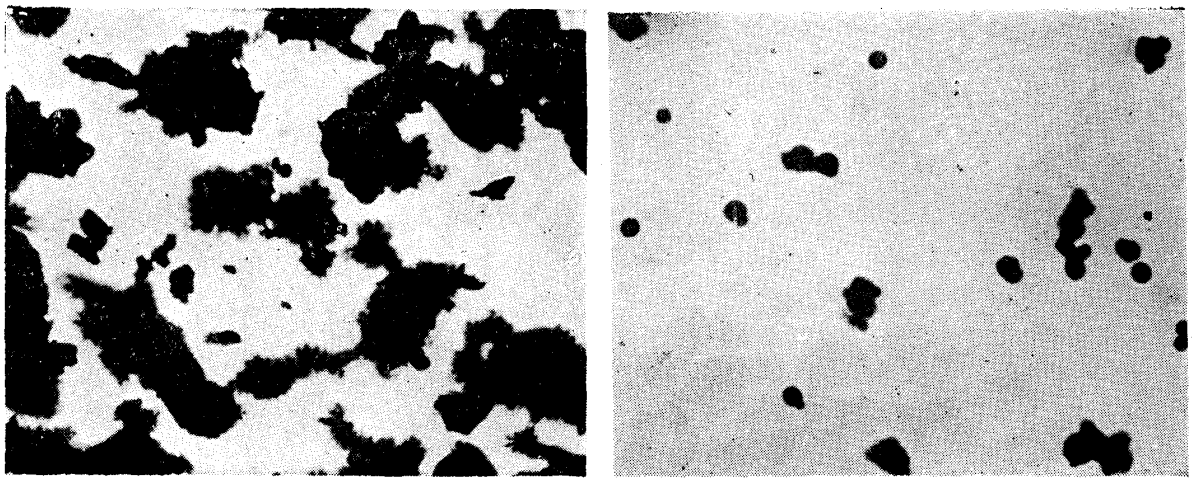
As for the powder of this metal, two sorts of powders were provided ; the one (A) was the powder reduced from the oxide by hydrogen, and the other (B) the carbonyl iron powder. Commercial reduced iron powder was used for the powder (A), Fig. 2 (A), but before preparing compact, it was re-reduced at 350°C for 3 hours in dried and purified hydrogen stream after passing through a 250 mesh screen, as it was slightly oxidized. Inspite of this cleaning treatment, 0.17 pct. of carbon remained, according to the result of a chemical analysis, and, therefore, strictly speaking, it was not iron powder, but steel powder. The powder (B) was carbonyl iron powder which was produced in our laboratory by decomposing the vapour of iron penta carbonyl ($Fe(CO)_5$). This green powder usually contains a considerable amount of free carbon just as produced. A part of free carbon in this powder remained even after it was reduced at 250°C for 2 hours in hydrogen stream, and a chemical analysis showed carbon content to be 0.35 pct. In this case, however,

(8) T. Okamura, K. Inagaki, Y. Masuda : Sci. Rep. RITU 2A (1950) 361.



(A) (B)

Fig 1. Silver Powder. ×400.



(A) ×400 (B) ×500

Fig 2. Iron Powder. Transmitted Light.

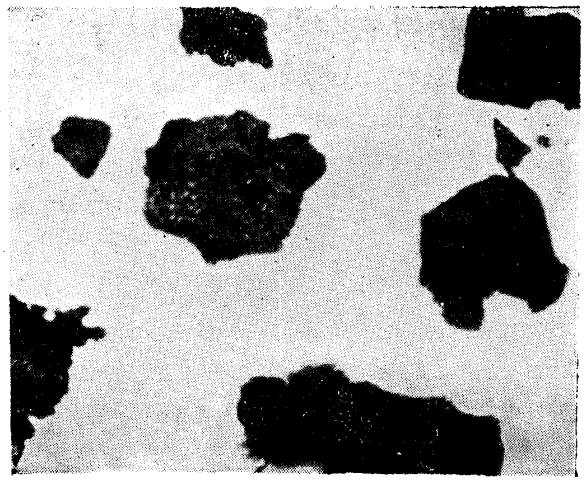


Fig 3. Nickel Powder. X400.

it was undesirable to carry out such a long decarburation treatment at higher temperature, since there was a fear of bringing a serious agglomeration of powder particle. After the decarburation treatment, the powder was poured into a glass bottle, containing hydrogen, in order to destroy partly coagulated powder, which remained even after the passing through a screen. Most of the particles of the powder (B) prepared in such a way was nearly spherical and less than 10 micron as shown in Fig. 2 (B).

Nickel :

The powder of this metal was also prepared chemically ; that is, first the nickel oxide was made by roasting the hydroxide precipitated by ammonium aqueous solution from a solution of nickel nitrate, which was prepared by dissolving the pellets of the Mond Nickel in nitric acid, and, subsequently, the oxide was reverted to metallic powder by reducing in dried and purified hydrogen stream. Before preparation of compact, a pre-reducing treatment at 500°C for 5 hours in hydrogen stream, was conducted with the powder, from which the coagulated was readily separated by means of passing through a 250 mesh screen. Though the conditions described above for this treatment were not so suitable to avoid the troublesome agglomeration and coarsening of particles, it was needed to expect a perfect reduction rate as possible.

The microphotograph of this powder is shown in Fig. 3.

Compacts

Silver :

For this metal, three series of compacts which were pressed at three different loads, respectively, and one series of the unpressed compacts were provided. As the latter specimens, 1.4 grs of the powder (A) was packed in a cylindrical quartz pipe, about 25 mm in length and about 5 mm in inner diameter, an end of which was closed by a patch of thin Indian paper. In order to make uniform the density of compact and to adjust it to a given value 2.6, after the quartz pipe was filled with powder, it was tapped on a wood plate by hand, until the filled powder settled down to a given height. This procedure was especially needed on account of a considerable effect of initial apparent density of compact upon sintering rate as indicated in later section. As for the pressed compact, about 5~7 grs of the powder (B) was used for a specimen, and formed in a steel die into a compact having a rectangular cross-section, 10 mm in length, 5 mm in width and about 3 mm in thickenss depending on the amounts of the load applied and of powder used. For two series of pressed compact, the pressing was carried out at 0.5 and 1 ton per sq. cm by hydraulic press, and for another series by hand-press at unknown load, less than 0.5 ton per sq. cm, and their green densities became 5.5, 6.5 and 7.3, according to the loads used. The amounts of powder used were adequately controlled, and "dwell time" of loading was always held in 30 seconds to give as the same

finishing dimension to the all compacts of whole series as possible.

Iron :

Two series of compacts were prepared for the powder (A) in the following ways. The first unpressed was made in the same way as the first series of silver powder, and 0.7 grs of the powder was used for a specimen, the green density of which was 3.5 ; the second was pressed at 2 tons per sq. cm., in the die already described, with 7 grs of the powder, and then the green density of the whole compact was made about 4.6 by careful application of load.

The carbonyl iron powder (B), on the other hand, was not so easy to be formed by pressing because of the spherical form of the particle, that only one series of unpressed compact was provided in the same way as described in the last paragraph. Though, also in this case, the same amounts of the powder as those of (A) was used for a specimen, on account of its' larger tap density, the green density of the compact became 3.7, which was a little larger than that of the compact (A).

Nickel :

For this metal compacts, the unpressed series, 0.4grs in weight and 2.1 in density, and the pressed at 2 tons per sq. cm, 4.2 in density were made, respectively, using only one sort of powder.

III. Results and Interpretations

1. Time Dependence in Sintering Rate

In this paper, the sintering process of compact was represented in terms of the fraction of total decrease in volume of voids in a compact, w, and the sintering time t. As already indicated in previous paper,[7]

$$w = \frac{(Vp - Vs)}{(Vp - Vm)}, \tag{1}$$

where Vp = apparent specific volume of green compact,

Vs = apparent specific volume of partial sintered compact,

Vm = specific volume of dense metal,

and all subsequent diagrams, where all data for w and t in each series with respective temperature were given with the scale of $\log w$ on the ordinate and $\log t$ on the abscissa.

Although the sintering time and temperatures are different for each series as noted in the diagrams, the measuring of the volume changes in compact with sintering progress were conducted in the same way as in the previous work.[7]

Silver :

For both series of (A) and (B), the sintering was carried out at given temperatures from 600°C to 800°C in the air, which could be neutral against silver at such temperatures, and the results were represented in Figs. 4, 5, 6 and 7, respectively.

Seeing these diagrams, it will be found that a simple power relation between w and t does not thoroughly appropriated for the whole process of densification, but, in fact, more complicated. After 30 minutes from the start of sintering, a linear relationship holds to the plotting of log w vs. log t for each sintering temperature, and they make a set of parallel straight lines. At least, in these range of sintering process, the densification rate can be expressed by the following equation :

$$w = At^n, \qquad (2)$$

where A is a constant depending on the temperature, and the power, n corrrespods to the slope of the straight lines. These isokinetic periods, however, usually appear later at lower temperature than at higher temperature. This change in the power n with sintering progress was found in all the cases of this work, and it seems to suggest that the power n depends on the geometrical configuration in a compact. Moreover, n varies more extensively with sort of metal powder than with the initial density of compaect, and in the least extent with the change of atmosphere.

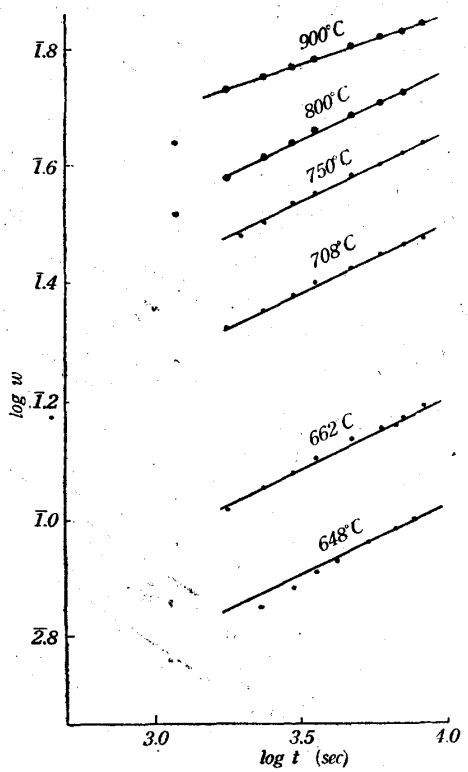


Fig. 4. Curves of log w vs. log t at given temperatures for silver powder compacts; unpressed, 2.6 in green density. in air.

As seen in Table I, $n=1/4$ for the series of unpressed compact, and $n=1/2.5$ for all of the pressed, while their initial densities are different from one another by more than 30 pct, according to the pressing load. This difference of densification rate between both pressed and unpressed compacts may be due to the geometrical characteristics of powder used here ; that is, for the latter series a flaky powder (A) was used and for the former a granular one (B), and, therefore, the geometrics in both compacts are quite different from one another. Furthermore, the same feature revealed also in the results for iron powder compact as shown in the following :

Iron :

In this case, the densification rate during sintering was compared in the same way between two series of unpressed compacts, which consisted of carbonyl and reduced iron powder, respectively. For the atmosphere of sintering a dried and purified hydrogen stream was chosen from a requirment of works at higher temperature than 1000°C. According to the results of our experimental work at higher temperature than 1000°C, any simple power relationship between w and t did

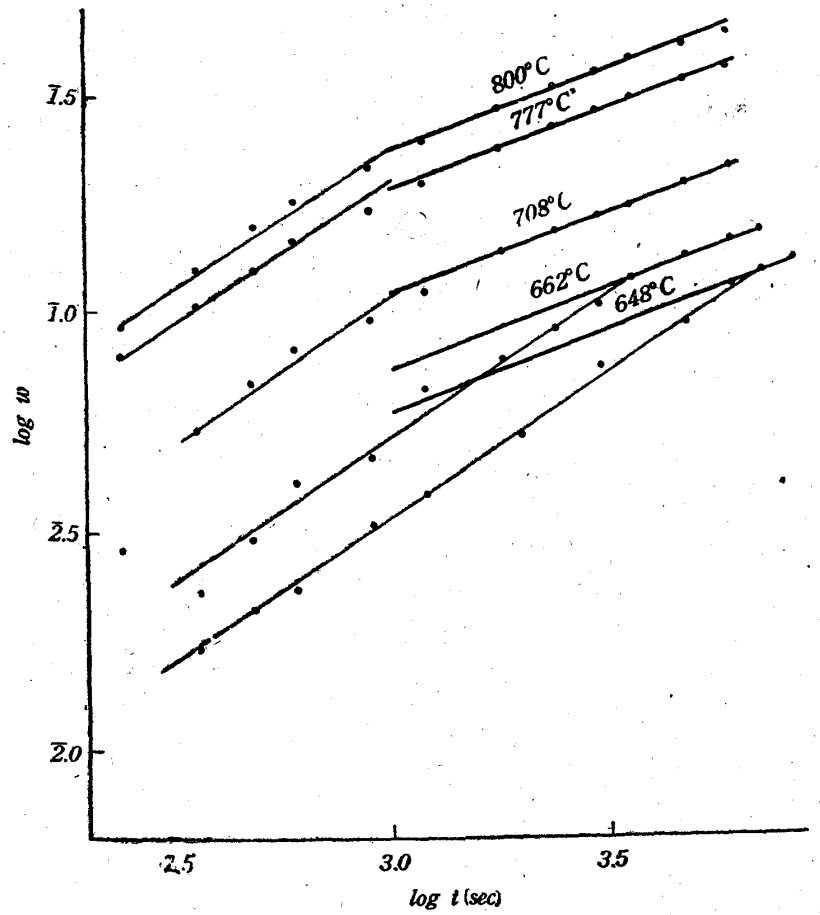


Fig. 5. Curves of log w vs. log t at given temperatures for silver powder compacts; pressed by hand press at an unknown load of less than 0.5ton per sq. cm, in air.

not hold at such a high temperature. A very high densification rate was usually observed for about 30 minutes at the beginning, and after passing through this period, the rate decreased abruptly and might even become negative in some cases, namely, "swelling". This swelling is, of course, due to the expansion of gases entrapped in isolated pores, and usually takes place in a sintering process at high temperature. Though it can be a considerable phenomenon in the powder metallurgical practice, in this paper, it was left out of consideration, since it was intrusive, rather unavailable, to know the mechanisms responsible for densification of compact during sintering. For this reason, only the results obtained at lower temperature than 1000°C, for both carbonyl and reduced iron compacts, are shown in Fig. 8 and 9, respectively. As seen in the both diagrams, the linearity for log w vs. log t is satisfied in some extent.

Form each diagram, $n=1/2.5$ and $n=1/5$ are given, respectively, for these two series of compacts, and a much greater rate of desification was observed for carbonyl iron powder compact than for reduced iron powder one. On the other

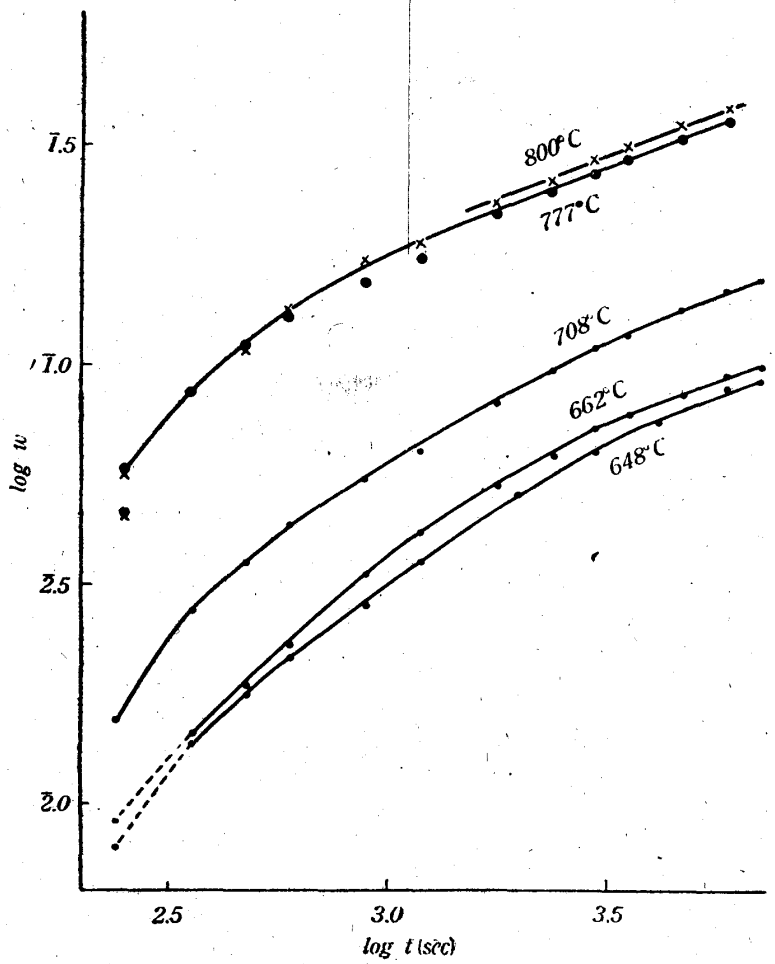


Fig. 6. Curves of log w vs. log t at given temperatures for silver powder compacts, pressed at 0.5ton per sq. cm, 6.5 in green density, in air.

hand, taking account of the small difference between both green densities of the two series' compacts, (as seen in Table I, it is only 5 or 6 pct, since they are 3.5 and 3.7, respectively) it cannot be considered, in fact, that such extensive difference of the densification rate in both series might be introduced by such a degree of difference between the green densities of both series' compacts ; rather, it will account for the difference in characteristics of powder particle, such as the geometrical form, size and other physical properties, on which the initial density of compact considerably depends.

These interpretation may be drawn also from the result obtained for a pressed compact at 2 tons per sq. cm., shown in Fig. 10*. In this case, despite an augmentation of 1.3 times in green density of compact against the preceeding case, and, moreover, using the same reduced iron powder, the power n remained 1/5, and

* This figure was cited from previous paper as a referrence.

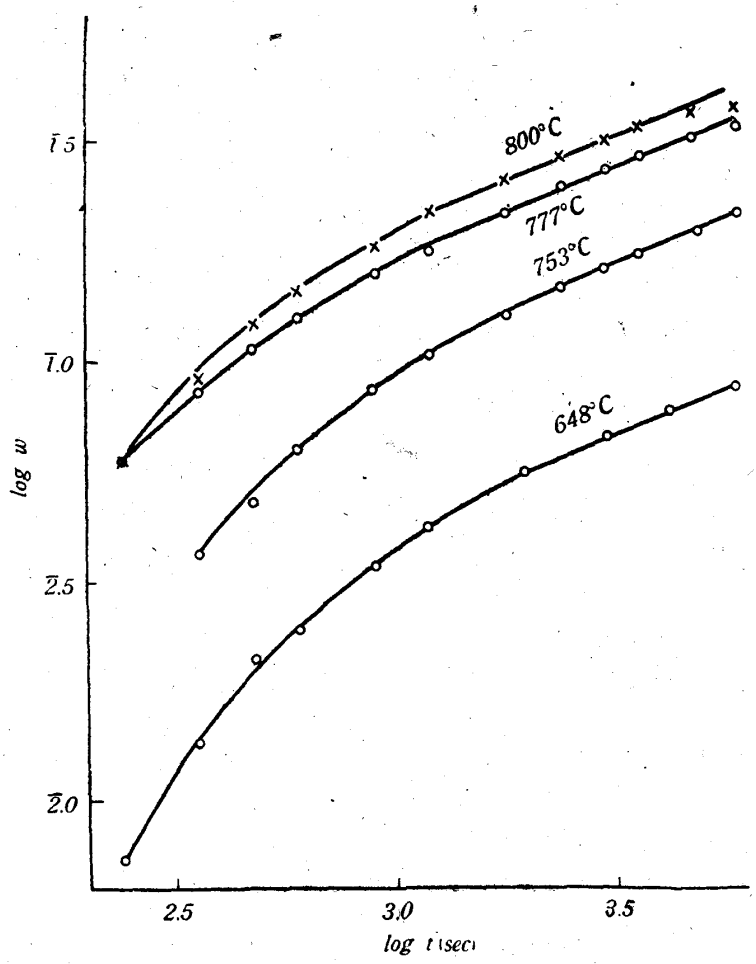


Fig. 7. Curves of log w vs. log t at given temperatures for silver powder compacts; pressed at 1 ton per sq. cm, 7.3 in green density, in air.

there was no remarkable enhancement in the densification rate. Although a strict comparison between these cases should be abstained because of the differ ence in atmosphere of sintering, it may seem a corollary of using the same characteristic powder.

In returning to the case of unpressed compact, there was found much differ ence in geometrical form, size and carbon content of the two kinds of powders as indicated in the last section. Since the first two of these characteristics should have a deep relation to the geometry in a compact, it seems plausible in this case, that the difference in desification rate between those powders is due to the geometrical characteristics of their particles. At present, however, we have no quantitative indication to formulate the relation between the rate of densification and the geometry in compact.

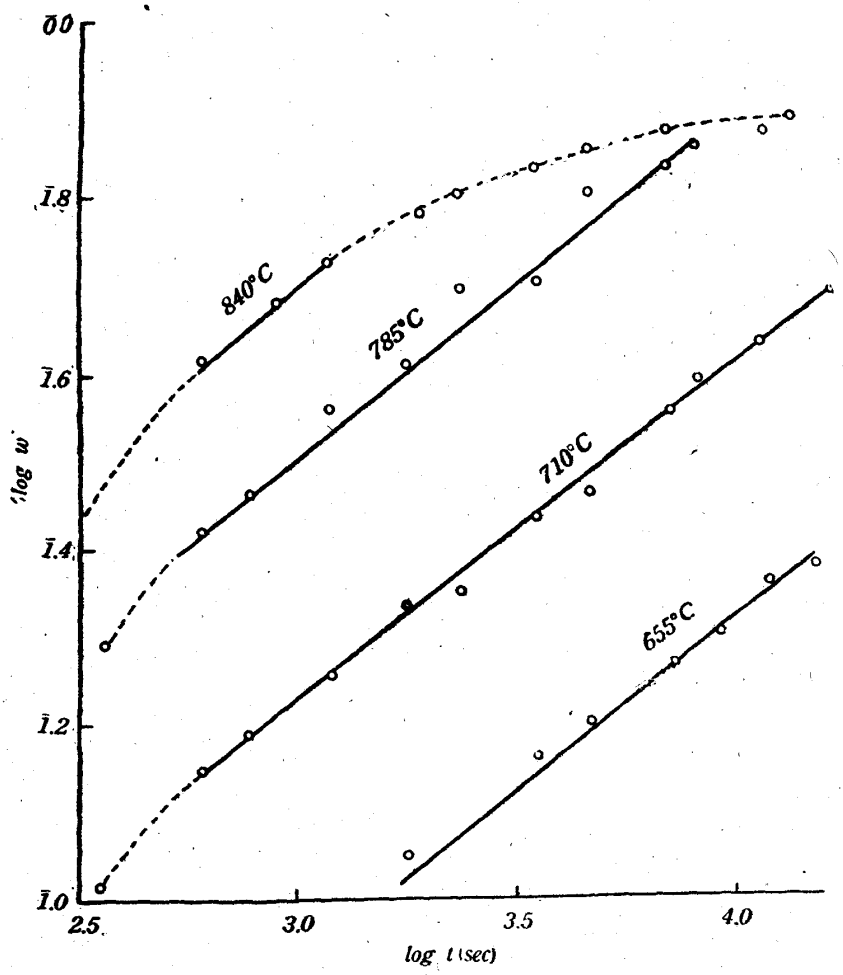


Fig. 8. Curves of log w vs. log t at given temperatures for carbonyl iron powder compacts, unpressed, 3.7 in green density, in hydrogen.

Nickel :

Since the works for this metal powder compact have not yet been completed, it seems to be not pertinent to publish our results in this paper, but in a way of a supplement to the present works, a few results obtained by this time are reported in the following.

The experiments were made for both compact, pressed and unpressed, in the same way as in the preceeding cases. The sintering operations were carried out at given temperatures from a minimum 770° C to a maximum 1200°C, in dried and purified hydrogen stream. The results for unpressed series are shown in Fig. 11. They form a set of parallel straight lines at least in a sintering duration of a fixed time interval, and in this case, the slope corresponds to 1/5. The results for pressed series at 2 tons per sq. cm. are plotted in Fig. 12 and 13 separately, according to the sintering temperature ; they correspond, respectively, to two groups below and above 1000°C. In comparing both diagrams, a

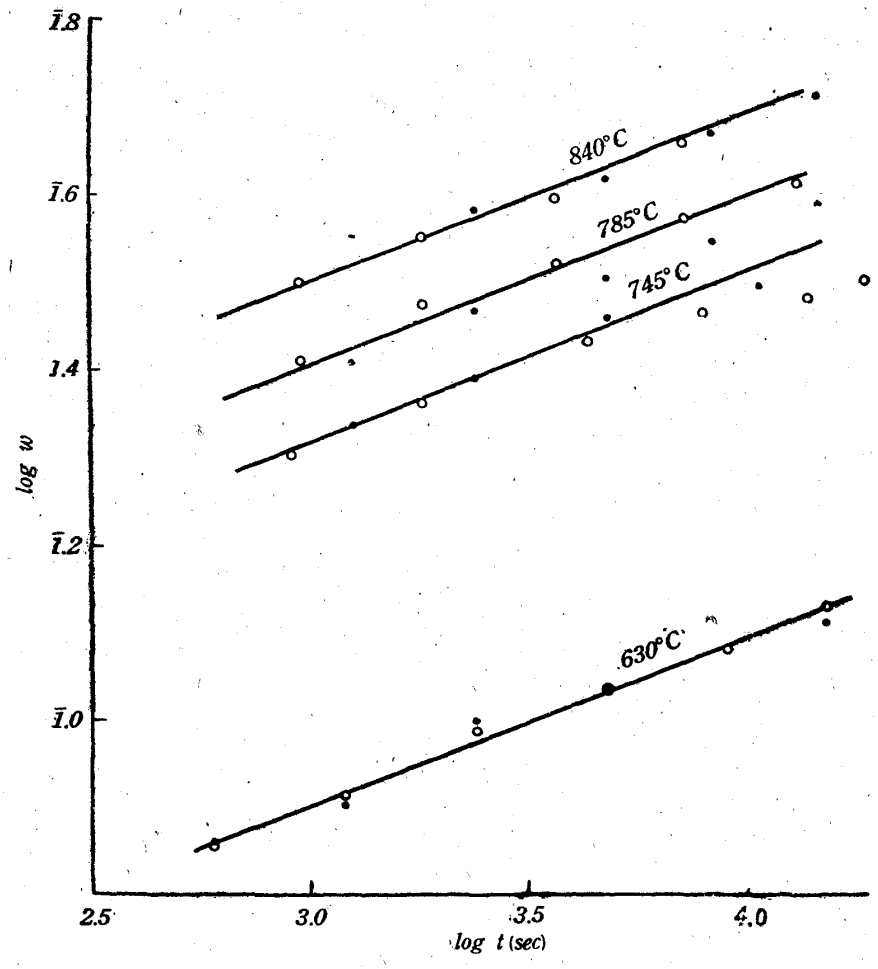


Fig. 9. Curves of log w vs. log t at given temperatures for reduced iron powder compacts, unpressed, 3.5 in green density, in hydrogen.

systematical discrepancy can be found clearly between their densification rates, namely, $n=1/3$ and $n=1/4$, respectively, below and above 1000°C. However, in this case, this was not due to the characteristics of the powder, because the same powder was used. At present, unfortunately, we can not answer definitely the question whether such change of n with temperature is occasional or not, for lack of systematic study concerning the effects of pressing load, or of initial density of compact, and of characteristics of powder upon the densification process. It should be noted, here, that there is a common nature of time dependence of densification rate in the whole cases, and that after long duration of sintering at lower temperature the value of n tends to that of earlier period at high temperature sintering. A possible interpretation of this result is that two compacts of same desity sintered at lower and higher temperature will have in itself a different geometric configuration to each other and it causes a change in densification rate. But this is only a speculation against a poor experimental

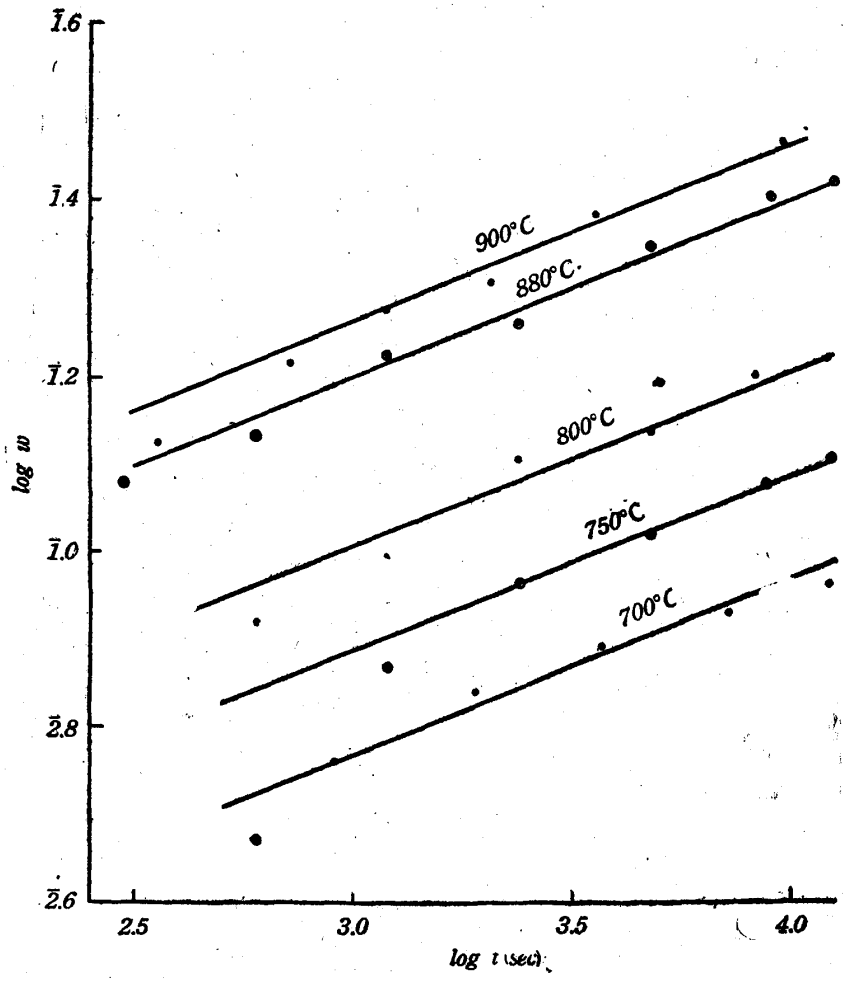


Fig. 10. Curves of log w vs. log t at given temperatures for reduced iron powder compacts, pressed at 2tons per sq. cm, 4.6 in green density, in vacuo (10^{-4}mm in Hg)

result obtained by this time, and it must be justified by futher experiments.

2. Temperature Dependence on Sintering Rate

As indicated in the previous paper, the rate of densification can be written in terms of w as follows, if a linear relationship between log w and log t holds over the range of time considered in these sintering operations:

$$\frac{dw}{dt} = Dw^{-p},$$

where D is a parameter of the rate of densification, depending on temperature.

According to our previous results of the experiment for copper and iron powder compact, the logarithm of parameter D was found to be approximately proportional to the reciprocal of absolute temperature, moreover, the activation heat estimated

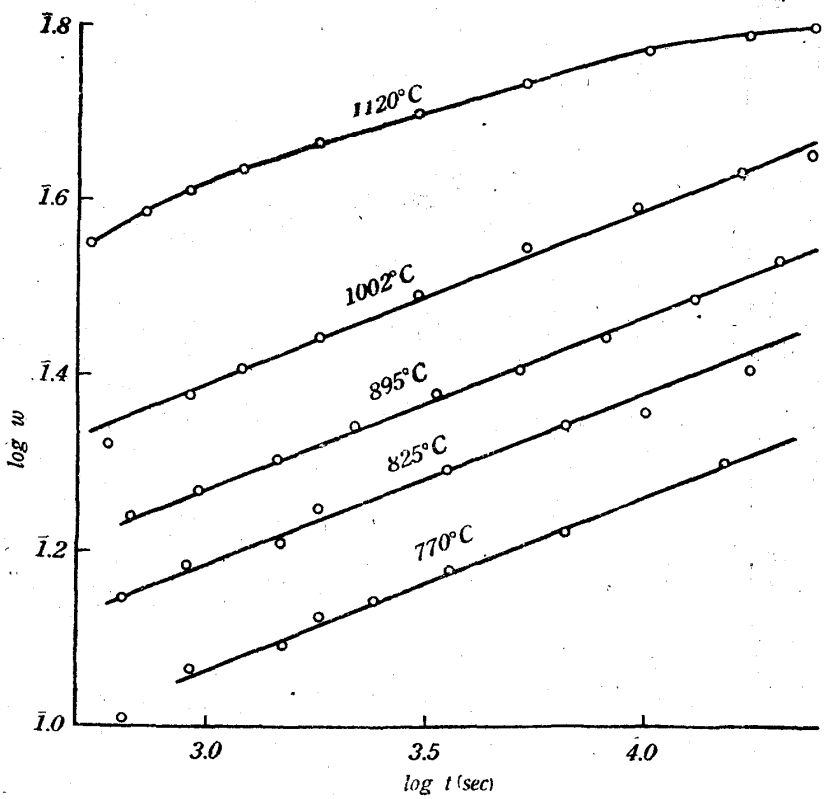


Fig. 11. Curves of log w vs. log t at given temperatures for reduced nickel powder compact, unpressed, 2.1 in green density, in hydrogen.

from the relation nearly corresponded to that of self-diffusion of the same metal atoms. In this section, such temperature dependence on sintering rate was re-examined one by one for the data described in the last section.

The plots for log D vs. $1/T$ obtained from the data in Figs. 4, 5, 6 and 7 are shown in Figs. 14, 15 and 16. As seen in these graphs, the whole plots fall into a straight line in each case, though the slope does not coincide with one another in all the cases. The activation heats which correspond to each slope of the straight lines are summerized in Table I. All the values and especially that of the powder (A) extremely exceeded 45.700 cal per mole which was determined by Kuczynski[2] from the experiment on binding rate between thin wire and plate of the same metal. At present, it is questionable whether these systematically higher activation heat are due to the oxidation of the substance by air, or not. It should be noted, however, that the same value of activation heat is given to the same powder, and there is no extensive change of the value with pressing load or green density of compact.

(9) C. E. Birchenall, R. F. Mehl: J. of Metals (1950) 144.

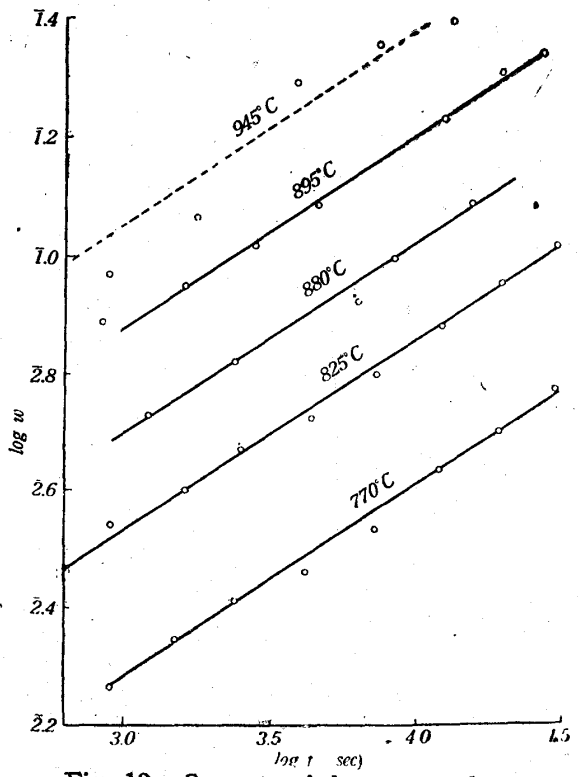


Fig. 12. Curves of log w vs. log t at given temperatures for reduced nickel powder compacts, pressed at 2 tons per sq. cm, 4.2 in green density, in hydrogen

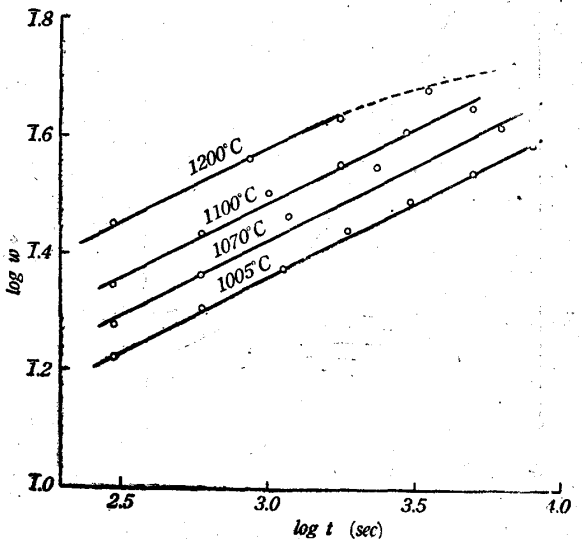


Fig. 13. Curves of log w vs. log t at given temperatures for reduced nickel powder compacts, pressed at 2 tons per sq. cm., 4.2 in green density, in hydrogen.

Iron :

In Fig. 17, the results for iron powder compact are summerized, and the values of activation heat are given in Table I. Among them, two values of the reduced iron powder are in good agreement with those obtained by Mehl and Birchenell[9] by means of the radioactive tracers method, whereas that of the carbonyl iron powder is comparable order of that for copper powder. In this case as well as in the case of silver, an intensive influence of characteristics of powder appeared on temperature dependence of densification rate, though it was questionable what kinds of characteristic factor of powder were respondible for the lowering of activation heat. The higher carbon content of this powder could have been responsible for it, but, on the other hand, in case of this powder, there was a possiblity that it might store a considerable free energy in the particle surface and interior as the result of the particular producing process[10]. If this is true, it seems plausible, in fact, that the excess free energy plays an important role in lowering apparent activation heat derived from the temperature dependence of parameter D, since the parameter D involves implicitly many terms of temperature depencence

(10) F. Skaupy : Metallkeramik, Verlag chem. Berlin (1943) 111.

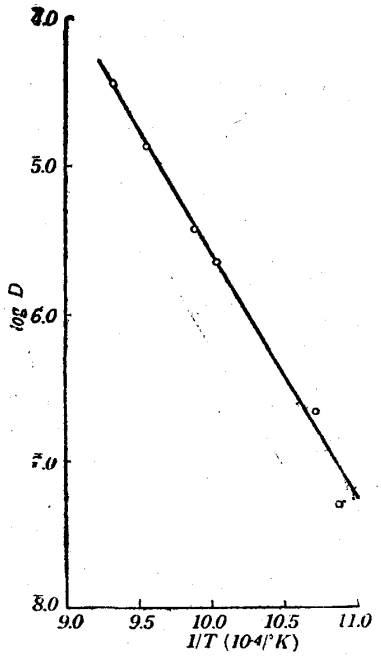


Fig. 14. Relation between rate parameter of densification and reciprocal of absolute temperature for silver powder compacts, unpressed.

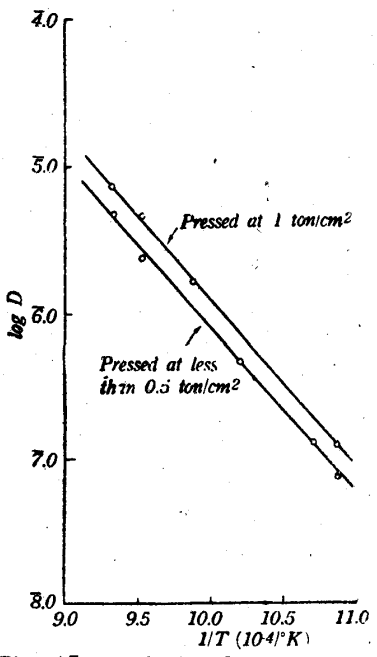


Fig. 15. Relation between rate parameter of densification and reciprocal of absoute temperature for silver powder compacts, pressed at 1 ton per sq. cm, and at less than 0.5 ton per sq.cm.

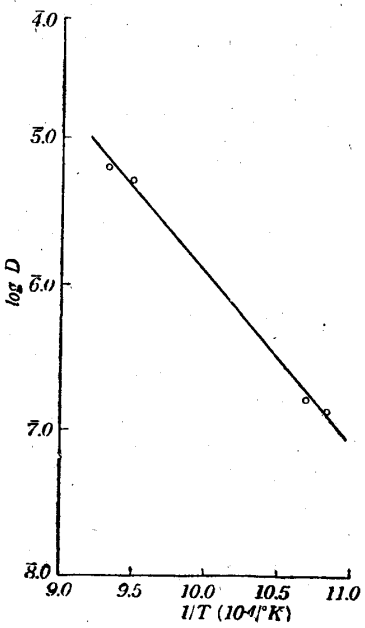


Fig. 16. Relation between rate parameter of densification and reciprocal of absolute temperature for silver powder compacts, pressed at 0.5 ton per sq. cm.

Table.

Powder	Preparation Method	Compacting Condition
Silver	Disintegrated by Stamp Mill.	Unpressed (tapped)
	Disintegrated by Eddy Mill.	Pressed by at unkown pressure less than 0.5 tons per sq. cm
	Disintegrated by Eddy Mill.	Pressed at 0.5 tons per sq. cm
	Disintegrated by Eddy Mill.	Pressed at 1 ton per sq. cm
Iron	Carbonyl	Unpressed (tapped)
	Reduced	Unpressed (tapped)
	Reduced	Pressed at 2 tons per sq. cm
Nickel	Reduced	Unpressed (tapped)
	Reduced	Pressed at 2 tons per sq. cm
	Reduced	Pressed at 2 tons per sq. cm

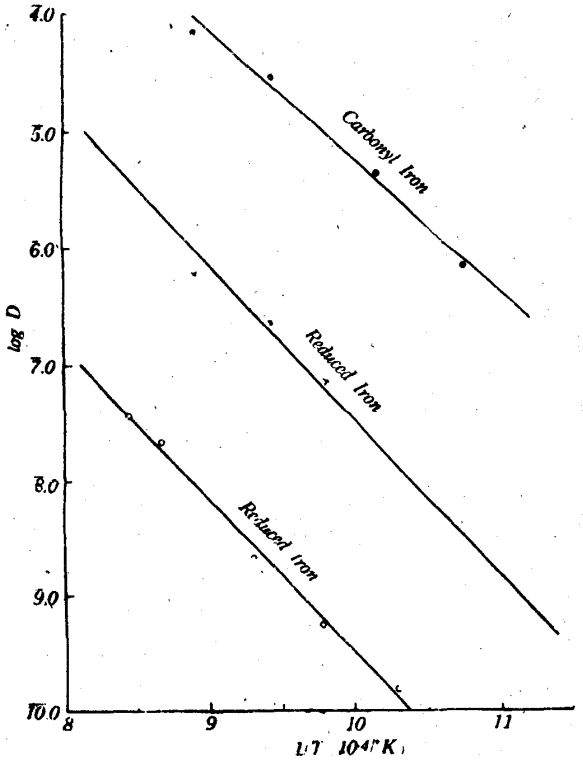


Fig. 17. Relation between rate parameter of densification and reciprocal of absolute temperature for various iron powder compacts.
● : for carbonyl iron powder compact, corresponding to Fig. 8.
× : for reduced iron powder compact, corresponding to Fig. 9.
○ : for reduced iron powder compact, corresponding to Fig. 10.

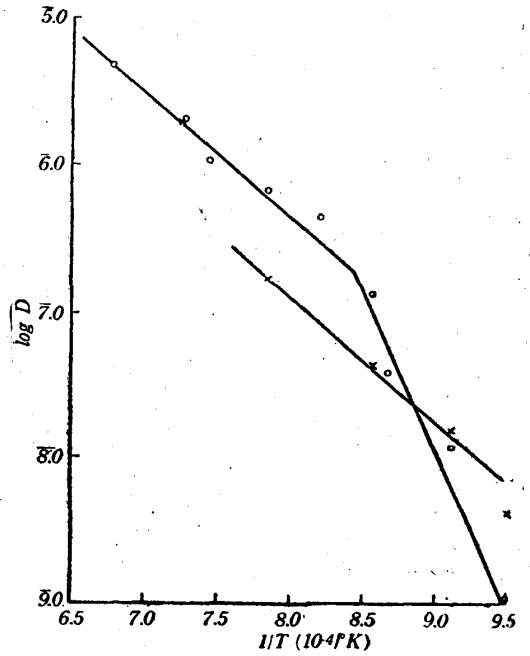


Fig. 18. Relation between rate parameter of densification and reciprocal of absolute temperature for nickel powder compacts, unpressed (×) and pressed at 2 tons per sq. cm (○).

I.

Green Density of compact	Sintering Atmosphere and Temperature range	n	Heat of activation cal. per mol.
2.6	Air from 648°C to 900°C	1/4	67,000
5.5	Air from 648°C to 800°C	1/2.5	51,400
6.5	Air from 648°C to 800°C	1/2.5	52,000
7.3	Air from 648°C to 800°C	1/2.5	52,000
3.7	Hydrogen from 655°C to 840°C	1/2.5	50,500
3.5	Hydrogen from 630°C to 840°C	1/5	65,000
4.6	Vacuum from 700°C to 900°C	1/5	65,000
2.1	Hydrogen from 770°C to 1102°C	1/5	42,000
4.2	Hydrogen from 770°C to 945°C	1/3	100,000
4.2	Hydrogen from 1005°C to 1200°C	1/4	42,000

such as driving force, and frequency of nuclei formation.

Nickel:

The plots of log D vs. log t for both pressed and unpressed series are summarized in Fig. 18.

In the series of unpressed compact, all the plots fall on a straight line, if an anomalous point ot high temperature is ignored.

As for the series of pressed compact, however, these plots do not fall on a straight line, but are rather separated in two groups, the one above 1000°C and the other below it. If the most probable two straight lines are drawn against each plot of the two groups, the activation heats corresponding to these slopes will be like those given in Table I., and those for the compact pressed and sintered at high temperature are about the same as those of the unpressed compact. This seems to show something about mechanism of densification of metal powder compact during sintering. However, in order to elucidate this, our experimental data for densification rate at higher temperature appears to be insufficient, and, therefore, in this paper any intepretation of this result has been reserved.

IV. Summary and Conclusion

From the present work concerning the rate of densification of various metal powder compact in sintering process, the following conclusions were drawn.

1. A simple power relation in reference to the rate of densification of metal powder compact, which was proposed in our previous paper, was applicable to all metal powders in this work (silver, iron nickel), at least in the range of steady sintering progress.

2. Rate of densification was not hold strictly to a constant value over all process of sintering; that is, it was fast at the beginning, and after passing through a long steady period, gradually went down.

3. Rate of densification was intensively influenced by characteristics of compact, and especially the geometrical configuration in a compact seemed to be a greatest determinant factor for the rate, except the effect of temperature.

4. Temperature dependence of the rate of densification was found to be approximately exponential to the reciprocal of absolute temperature for all those metal powders, at least in a given temperature range. However, there was found a systematic deviation from this relation at higher temperature.

5. Apparent activation heats for densification of those metal powder compacts obtained in this work were roughly of the same order as those of self-diffusion of those metal atoms.

6. The effect of pressing load or initial density of compact and of sintering atmosphere upon the values of apparent activation heat was found to be almost negligible.

7. For different powders of same metal prepared by different procedures into different forms, extensively different activation heats were obtained.

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